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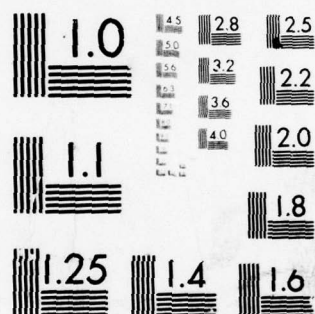
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THE CORROSION BEHAVIOR AND RUTHERFORD  
BACKSCATTERING ANALYSIS OF PALLADIUM  
IMPLANTED TITANIUM

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G. K. HUBLER AND E. McCafferty

ADVANCED MATERIALS TECHNOLOGY BRANCH  
MATERIAL SCIENCE AND TECHNOLOGY DIVISION

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three orders-of-magnitude for Pd implanted samples. The corrosion potential-time curves and high resolution RBS data both show that soon after immersion, the Pd surface concentration rises to 20 atomic percent because of preferential dissolution of Ti and that the Pd is retained in the surface for corrosion times of up to 9 hr. The steady state corrosion potential of implanted samples is close to that of pure Pd and 800 mV anodic with respect to the corrosion potential of pure Ti. The protection is explained by the fact that the mixed electrode potential is more noble than the critical potential for passivity of Ti, resulting in a markedly reduced dissolution rate.

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THE CORROSION BEHAVIOR AND RUTHERFORD BACKSCATTERING  
ANALYSIS OF PALLADIUM-IMPLANTED TITANIUM

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ABSTRACT

The corrosion behavior of Pd implanted Ti in boiling 1 Molar sulfuric acid has been investigated by means of high resolution Rutherford backscattering (RBS) profiles of the Pd concentration as a function of corrosion time, and by electrochemical methods consisting of corrosion potential versus time curves and potentiostatic polarization data. Employing ion-implanted Xe as a surface "marker", absolute corrosion rates were determined by RBS analysis and compared to corrosion rates determined from the polarization curves. The rate of Ti dissolution is found to be reduced by about three orders-of-magnitude for Pd implanted samples. The corrosion potential-time curves and high resolution RBS data both show that soon after immersion, the Pd surface concentration rises to 20 atomic percent because of preferential dissolution of Ti and that the Pd is retained in the surface for corrosion times of up to 9 hr. The steady state corrosion potential of implanted samples is close to that of pure Pd and 800 mV anodic with respect to the corrosion potential of pure Ti. The protection is explained by the fact that the mixed electrode potential is more noble than the critical potential for passivity of Ti, resulting in a markedly reduced dissolution rate.

## INTRODUCTION

Corrosion of metals is caused by chemical or electrochemical reactions occurring within the first few atomic layers of the surface. One method of corrosion control is to introduce by alloying, elements which improve the thermodynamic stability of the surface or promote the formation of passive films. A disadvantage of this method is that elements which improve corrosion resistance may not be those which give the desired structural properties of the material. Ion implantation of metals offers the capability of modifying the surface chemically without affecting bulk physical or mechanical properties, because implantation depths are typically only 1 to 1000 nm (10 to 10,000 Å). Other attractive features of the ion-implantation method and additional background has been given by Ashworth and co-workers.<sup>1</sup>

Results in the literature pertaining to the effect of ion implantation on the aqueous corrosion of metals has been directed toward iron and its alloys. Ashworth et al. found that Cr implanted into Fe to surface concentrations of up to 6% Cr produced the same corrosion resistance as bulk 6% content alloys.<sup>2</sup> In addition, it was found that ion implanted Ta was better than Cr in improving the corrosion resistance of Fe.<sup>3</sup> The Ta in Fe system had not been previously studied in bulk alloys because of the vanishingly small solid solubility of Ta. Covino and co-workers<sup>4,5</sup> studied Cr and Ni implanted into Fe and obtained similar results.

This paper reports on the corrosion behavior and characterization of Pd-implanted titanium in boiling 1M sulfuric acid. It is well known that small amounts of Pd in bulk alloys (0.1 atomic percent) produce a dramatic reduction in the corrosion rate of titanium in boiling acids.<sup>6,7</sup>

The present investigation utilizes electrochemical techniques in conjunction with high resolution Rutherford backscattering measurements. Employing ion-implanted Xe as a surface "marker", absolute corrosion rates were determined by Rutherford



backscattering (RBS) analysis. These rates were in good agreement with the corrosion rates determined from the polarization curves and by colorimetric measurements of dissolved Ti. The rate of Ti dissolution is shown to be reduced by about three orders-of-magnitude for Pd implanted samples. The protection is explained by retention of surface Pd producing a mixed corrosion potential which is above the critical potential for passivity of Ti, resulting in a markedly reduced dissolution rate.

Preliminary results of this investigation have been published elsewhere.<sup>8,9</sup>

### EXPERIMENTAL PROCEDURE

In order to obtain unambiguous high-resolution depth information concerning the ion implanted palladium, it is necessary to prepare smooth and clean titanium surfaces. Therefore, careful attention was given to the preparation of the original titanium surfaces by means of a mechanical polishing procedure. Samples of 5 mm thickness were cut from the titanium rod (99.97% pure, 1.0cm diameter) and were vacuum mounted in epoxy leaving one exposed surface to be polished. The exposed face was abraded with 240-, 320-, 400-, and 600-grit silicon carbide polishing papers, followed by a mechanical polish with 6-  $\mu\text{m}$  diamond paste on cloth. A final polish with 0.05  $\mu\text{m}$   $\gamma\text{Al}_2\text{O}_3$  particles in a 5% oxalic acid solution<sup>10</sup> resulted in a mirror finish surface in which no scratches or surface features could be detected on a scanning electron microscope (SEM) at magnifications up to 10,000 times.

Surfaces polished in this manner were implanted with Pd to a fluence of  $1 \times 10^{16}$  ions/cm<sup>2</sup> at an energy of 90 keV. This fluence resulted in a near-gaussian shaped concentration profile centered at a depth of 24nm (240 Å). The concentration at the gaussian peak was 4 atomic percent, and the concentration of Pd at the surface was less than 0.1 atomic percent. Some samples were also implanted with Xe to a fluence of  $3.5 \times 10^{15}$  ions/cm<sup>2</sup> at 90 keV. The Xe concentration profile was similar to the Pd profile but with a factor-of -three lower peak concentration. The Xe atoms provided a "marker"

in RBS analysis with which to register the amount of Ti removed from the front surface. It is assumed that the Xe atoms dissolve into solution as they are uncovered. The amount of Ti removed is measured as a shift toward the surface of the RBS Xe profile. (Of course, physically the surface moves in the direction of the Xe atoms as the Ti dissolves.) The behavior of Pd implanted, and Pd plus Xe implanted samples was identical in both RBS and electrochemical measurements.

High resolution RBS profiles were obtained with a 2.5 MeV  $\alpha$ -particle beam produced by the NRL 5MV Van de Graaff accelerator. Particles backscattered by the target at an angle of  $135^\circ$  were detected in a position-sensitive detector placed in the focal plane of a 50.8cm by  $180^\circ$  double - focusing magnetic spectrometer. This particle detection system provides an energy resolution of 0.08% which results in a system depth resolution of about 40 Å. Details of the RBS technique and the magnetic spectrometer detection system may be found elsewhere.<sup>11</sup>

Electrochemical measurements were made using a single-compartment cell fitted with a condenser. The cell was also fitted with standard taper ports for insertion of the sample electrode, auxiliary electrode, and a second, smaller condenser through which aliquots of the solution were pipetted for colorimetric analysis of dissolved titanium by the hydrogen peroxide method.<sup>12</sup>

Electrode potentials were measured versus the mercury/mercurous sulfate electrode using a Luggin-Haber capillary. Heat conduction through the capillary was sufficient to maintain the external reference electrode at  $95^\circ$ , as compared to the cell temperature of  $100^\circ$ . The Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrode was utilized because it has been shown to be a reliable reference electrode at those temperatures.<sup>13</sup> All electrode potentials in this paper are reported relative to the Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrode. (Potentials are converted to the NHE scale by adding 0.66V).

Before use, the electrochemical cell and all component glass parts were cleaned with a sulfuric acid/nitric acid mixture and were washed thoroughly with tap and then



distilled water. Solutions of 1 M sulfuric acid were made from the reagent grade chemical and distilled water prepared in a Barnstead still.

## RESULTS

Samples co-implanted with Pd and Xe were immersed in boiling 1M H<sub>2</sub>SO<sub>4</sub> for various times, removed from the solution, and profiles of the Pd and Xe concentrations measured. Figure 1 shows profiles for an as-implanted sample corroded for the times of 6, 12, 48, and 420 min. The Ti surface with respect to the Pd and Xe profiles are shown as vertical dashed lines in the figure. After 6 min a significant shift of both the Pd and Xe profiles is evident. After 12 min the Xe signal has diminished and the Pd has clearly redistributed. For longer corrosion times the Xe signal continues to diminish while the Pd profile shows that Pd builds up on the surface to a concentration of about 20 atomic percent. The total area beneath the Pd profile for all corrosion times is constant to within the  $\pm 5\%$  error in the measurement indicating that no Pd has been removed from the surface. The continual reduction of the Xe signal with corrosion time, however, indicates that Ti is being dissolved. Note that after 420 min, some Xe still remains in the sample.

Figure 2 shows similar profiles for samples implanted with Xe only. Fifty percent of the Xe is removed after 65 sec, 90% is removed after 110 sec and 100% removed after 240 sec.

Profiles of implanted samples that were annealed at 101°C for several hours showed that there is no bulk diffusion of Pd or Xe at this temperature. Therefore, the increased surface concentration of Pd and the loss of Xe occur due to the dissolution process and cannot be attributed to diffusion effects.

Implanted Pd is retained at the surface for at least 9 hr, the longest test performed to date. Longer tests were precluded because of the failure of the epoxy molds. This retention time was verified by colorimetric analysis of dissolved titanium as

a function of immersion time. As seen in fig. 3, a negligible amount of titanium was lost from the Pd-implanted sample until after immersion for 8 hr.

Figure 4 shows electrode potentials for pure titanium, pure palladium, and palladium-implanted titanium as a function of immersion time in boiling (100°C) 1 M sulfuric acid. The time-axis is plotted logarithmically for illustration purposes only. The steady-state open-circuit corrosion potential of palladium was approximately 1000 mV more noble than that of pure titanium. The steady-state corrosion potential of implanted sample was much closer to that of pure palladium than of pure titanium.

In the first few minutes of immersion, the implanted samples show a rapid transition in time from a corrosion potential near that of pure Ti to a potential close to pure Pd. The initial part of this transition is shown in Figure 5. After 1 minute in the case of two of the implanted samples and after 1.5 minutes for a third, the electrode potential was  $-1.0 \text{ V vs Hg/Hg}_2\text{SO}_4$  and tending toward the potential of pure titanium. In the next few seconds in each case, however, the electrode potential reversed toward the noble direction as the Ti-rich surface dissolved away to expose a new surface region containing an increased concentration of Pd. According to the RBS data, the surface concentration of Pd is initially less than 0.1% in as-implanted samples, rises to 5% after 6 min, 10% after 12 min and saturates at about 16% after 48 min.

Figure 6 shows potentiostatic anodic polarization curves for pure titanium, pure palladium, and palladium-implanted titanium in boiling 1 M  $\text{H}_2\text{SO}_4$ . All curves were determined after steady-state open circuit potentials were first established (2 to 2-1/2 hr immersion). For a given potential, the anodic current was usually constant within 5 to 10 min. The anodic curve for pure titanium shows the normal active-passive behavior which has been typically observed.<sup>6,7,14</sup> Well-defined Tafel slopes were not observed in the active region but the corrosion rate at the open-circuit potential, as determined by the colorimetric analysis data in Fig. 3, is  $3.7 \text{ mA/cm}^2$ , on the basis that the overall anodic reactions is  $\text{Ti} \rightarrow \text{Ti}^{+3} + 3\text{e}^-$ .<sup>14</sup> The implanted samples display a passive current density

of 2 to 6  $\mu\text{A}/\text{cm}^2$ . The approach to the passive current plateau is very rapid, so that we are probably not too much in error by assuming that the passive current is also the corrosion current at the open-circuit potential of the implanted sample. Thus, implantation with Pd lowers the corrosion rate of Ti by a factor of about 1,000.

Anodic current densities for pure Pd are less than the values for the implanted samples for electrode potentials more negative than 0.2 volts vs  $\text{Hg}/\text{Hg}_2\text{SO}_4$ . At potentials more positive than + 0.2 volts, the corrosion rate of the implanted sample is less than that of pure Pd, as seen in Fig. 6. Using the Pourbaix diagram<sup>15</sup> for palladium at 25°C as an approximate guide, at zero pH Pd is polarized from a region of immunity into one of corrosion for potentials more positive than 0.81V vs NHE (0.15V vs  $\text{Hg}/\text{Hg}_2\text{SO}_4$ ).

Corrosion rates were also determined in a novel manner from the RBS profiles in Figs. 1 and 2. Fig. 7 shows the amount of Ti removed from the implanted sample as a function of corrosion time, as measured by energy shifts in the Xe profiles. These measurements are obtained in the following manner. It is assumed that the shape of the Xe profile is modified only by the removal of Xe atoms from the surface as the surface moves inward. The shift in energy of the remaining Xe profile with respect to the initial profile is converted into a thickness of material removed by means of the well known energy loss rate ( $dE/dx$ ) for He ions in titanium. For example, 2.5 MeV He ions incident on the sample that are scattered by a Xe atom and are subsequently detected have an effective  $dE/dx = 0.09 \text{ keV}/\text{\AA}$ . If an energy shift of 10 keV is measured in the Xe profile, the thickness of material removed,  $t$ , is  $t = 10 \text{ keV}/0.09 \text{ keV}/\text{\AA} = 111 \text{ \AA}$ . By this method, the Ti corrosion rate is determined by the slope of the curve in Fig. 7, which is seen to be very large at small corrosion times, but for corrosion times greater than one hr becomes constant at  $0.0044 \text{ \AA}/\text{sec}$ . This value may be considered the steady-state corrosion rate because the Pd profiles in Fig. 1 indicate that the Pd redistribution is complete for times greater than about one hr. Also, the open circuit corrosion potential is also nearly



constant at this time, as seen in Fig. 4. The rate of Ti removal of  $0.0044 \text{ \AA/sec}$  corresponds to a corrosion current density of  $1.2 \text{ \mu A/cm}^2$ , in reasonable agreement with the values measured by the polarization method. The values are listed in Table I.

The behavior of Xe-only implanted samples is shown in Fig. 8. The circles are for samples which were at room temperature when inserted into the boiling acid. There is an incubation period of 30 to 60 seconds during which there is negligible removal of Ti. This incubation is probably caused by two effects. First, some time is required to remove the native oxide film from the metal surface; and secondly, the sample mass (i.e. epoxy + Ti) requires time to warm up from room temperature to  $101^\circ\text{C}$ , the boiling temperature of  $1 \text{ M H}_2\text{SO}_4$ . The latter effect can be minimized by preheating the samples in boiling distilled water and quickly transferring the sample to the acid solution. The procedure reduced the incubation time to about 20 sec as shown by the crosses in Fig. 8. However, preheating the sample quite possibly introduces another variable in that the native oxide may thicken during the preheating. Also the thickening of air formed oxides occurs as the result of ion implantation in  $\text{Fe}^{16}$  and may occur for Ti as well. However, the slope of the solid line in Fig. 8 is  $22 \text{ \AA/sec}$ , in good agreement with the value of  $14 \text{ \AA/sec}$  determined by colorimetric analysis of dissolved titanium. When the same slope is drawn for the case of insertion at room temperature, the incubation period is seen to be 50 seconds, in good agreement with the delay time required in Fig. 4 for Ti to approach its steady state corrosion potential.

#### DISCUSSION

The corrosion resistance of the Pd-implanted surface alloy in boiling  $1\text{M}$  sulfuric acid is comparable to that of bulk Pd/Ti alloys. Table II shows that the corrosion rate of the ion-implanted system is actually less than the corrosion rates of the bulk alloys, most likely due to the greater surface concentration of Pd in the ion-implanted case. Table II also shows that the corrosion rate of unimplanted titanium agrees favorably with the

results of previous investigators.

Electrochemical measurements and Rutherford backscattering analyses indicate that the improvement with the implanted sample is due to initial preferential dissolution of titanium with subsequent buildup and retention of surface palladium. The role of Pd is to provide cathodic sites for the hydrogen evolution reaction. As the surface concentration of Pd increases, so does the cathode/anode area ratio. The electrochemical behavior of the composite electrode is determined by the intersection of the polarization curves for hydrogen evolution on the cathodic Pd sites and dissolution of Ti on the anodic sites.

The observed mixed potential of  $-0.35$  V resides in the passivation region of Ti, resulting in a markedly reduced dissolution rate. This mechanism was first proposed for noble metal alloying of bulk titanium by Stern and Wissenberg.<sup>6</sup>

According to the Rutherford backscattering analyses, the concentration of Pd at the surface is increased to about 20% by the initial preferential dissolution of Ti. A measurement by X-ray photoelectron spectroscopy (XPS) on a sample after a 5 hr immersion showed about equal amounts of Pd and Ti on the surface implying a Pd surface coverage of 50%. In addition, it was determined that the Ti was in the form of an oxide with the oxygen being 3 to 4 times more abundant than Ti. There is good qualitative agreement between the two measurements of surface coverage of Pd. Quantitative agreement is precluded by uncertainties involved in each measurement technique. For example, computer simulations of RBS energy spectra show that with a  $40 \text{ \AA}$  depth resolution, a  $50 \text{ \AA}$  thick, 20% Pd coverage cannot be distinguished from a  $5 \text{ \AA}$  thick 50% coverage overlying a  $45 \text{ \AA}$  thick, 16.7% coverage.

A further complication in measuring the anode/cathode area ratio arises due to different effective surface areas of the implanted versus unimplanted samples. Figure 9 shows optical photographs and micrographs taken with the scanning electron microscope (SEM). The optical photographs (top) were exposed by scattered light from the sample



surface, resulting in dark images for the mirror finish surfaces (implanted samples before and after corrosion). The bright image from the unimplanted, corroded sample (middle) shows that the surface is very rough because of the large amount of diffuse scattering. The surfaces are shown in more detail by their corresponding SEM micrographs (bottom). The two implanted samples are smooth and featureless, while the unimplanted sample surface is very granular and pitted. The effective surface area of the unimplanted sample is somewhat larger than for the implanted, smooth surfaces. A reasonable estimate is that the surface roughness is two or three times that of the implanted sample.

Fig. 10 shows the cathodic polarization curve for hydrogen evolution on bulk palladium and portions of the anodic polarization curve for bulk titanium. These curves are computed on the basis of equal areas of Pd and Ti, and show the total current which would be realized for the two electrochemical processes occurring on an implanted sample having a 50% Pd enrichment. Allowing a surface roughness factor of 2 to 3 for the anodic Ti curve, the two curves intersect at an electrode potential of -0.42 to -0.46 V, and a corrosion current density of 2.3 to 6.0  $\mu\text{A}/\text{cm}^2$ . These values are not too different from the corrosion potential (-0.26 to -0.35 V) and corrosion rates (2 to 6  $\mu\text{A}/\text{cm}^2$ ) of the implanted sample. Thus, the electrochemical behavior of the implanted sample can be reasonably interpreted by the mixed potential corrosion theory.

No evidence of intermetallic surface compounds of Ti and Pd was found upon examination of the implanted surface using glancing angle electron diffraction.

### CONCLUSIONS

The active dissolution of titanium in boiling 1M  $\text{H}_2\text{SO}_4$  is reduced by three orders-of-magnitude when implanted with 1.8  $\mu\text{g}/\text{cm}^2$  of Pd in a thin surface layer, and the corrosion protection lasts for at least 9 hr. The mechanism of corrosion protection is explained by the fact that Pd residing on the surface creates a highly local galvanic couple whose corrosion potential is between that of pure Pd and pure Ti, and is more

noble than the critical potential for passivity of Ti. This corroborates the mechanism proposed by other workers on Ti-Pd alloy systems.

A method of determining absolute corrosion rates by measuring energy shifts of an implanted Xe "marker" in RBS measurements gave results in good agreement with electrochemical methods.

Both RBS and potential vs time measurements show that initially the Pd is buried beneath the surface, and preferential dissolution of Ti redistributes Pd until a high surface concentration is obtained ( $\sim 20\%$ ). The approximately equal areas of anode and cathode material are then responsible for the noble value of the corrosion potential of implanted samples.

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## Figure Captions

- Fig. 1. The energy spectrum of  $\alpha$  particles backscattered from ion-implanted Pd and Xe in pure Ti metal for an as-implanted sample, and after four different times of immersion in boiling 1M  $\text{H}_2\text{SO}_4$ . Particle energy is converted into a depth scale on the abscissa.
- Fig. 2. The energy spectrum of  $\alpha$  particles backscattered from ion-implanted Xe in pure Ti metal for an as-implanted sample (top), after immersion in boiling 1M  $\text{H}_2\text{SO}_4$  for 65 sec (middle), and 110 sec (bottom). Particle energy is converted into a depth scale on the abscissa.
- Fig. 3. Corrosion-time curves for titanium and palladium-implanted titanium in boiling 1M  $\text{H}_2\text{SO}_4$ , as measured by colorimetric analysis of dissolved titanium. The sharp increase in dissolved titanium after approximately 8 hr was caused by failure of the epoxy mold.
- Fig. 4. Open-circuit corrosion potentials as a function of immersion time in boiling 1M  $\text{H}_2\text{SO}_4$  for pure titanium, pure palladium, and palladium-implanted titanium. The different symbols refer to replicate experiments.
- Fig. 5. Initial portions of the electrode potential-time curves for titanium and palladium-implanted titanium in boiling 1M  $\text{H}_2\text{SO}_4$ .
- Fig. 6. Anodic polarization curves for titanium, palladium, and palladium-implanted titanium in boiling 1M  $\text{H}_2\text{SO}_4$ .
- Fig. 7. Rutherford backscattering measurements of the thickness of Ti removed from a Pd implanted Ti sample as a function of corrosion time in boiling 1M  $\text{H}_2\text{SO}_4$ .
- Fig. 8. Rutherford backscattering measurements of the thickness of Ti removed from pure Ti samples as a function of corrosion time in boiling 1M  $\text{H}_2\text{SO}_4$ .
- Fig. 9. Photographs of epoxy mounted Ti samples (top) and their corresponding



SEM micrographs (bottom). All sample were intially polished to a mirror finish. The photographs detected mostly diffusely scattered light and indicate that the center sample has a very rough surface.

Fig. 10. The cathodic polarization curve for hydrogen evolution on Pd and portions of the anodic polarization curve for Ti in boiling 1M  $\text{H}_2\text{SO}_4$ . Both curves are calculated on the basis of equal electrode areas of Pd and Ti. (Duplicate experimental runs are shown for each curve).

Table I.

Corrosion rates for titanium and palladium-implanted titanium in boiling 1M  $\text{H}_2\text{SO}_4$ .

Sample	Corrosion Rate		Method of Determination
	Corrosion Current Density	Rate of Titanium Removal	
Titanium	3.7 mA/cm <sup>2</sup>	14 Å/sec	Colorimetric analysis of solution
	6.0 mA/cm <sup>2</sup>	22 Å/sec	RBS profiles
Pd-implanted Titanium	2-6 µA/cm <sup>2</sup>	0.0074 to 0.022 Å/sec	Polarization curves
	1.2 µA/cm <sup>2</sup>	0.0044 Å/sec	RBS profiles

Table II.  
Comparison of experimental corrosion rates in boiling 1 M H<sub>2</sub>SO<sub>4</sub>.

Investigator(s)	Pd Content	Corrosion Rate in Å/sec		
		Ti	Pd/Ti Alloy	Pd-implanted Ti
Tomashov et al. <sup>7</sup>	0 wt.%	77		
"	0.1		2.2	
"	2.0		0.49	
Cotton <sup>17</sup>	0	19		
Stern and Bishop <sup>18</sup>	0	32		
"	0.22		0.54	
Stern and Wissenberg <sup>6</sup>	0	32		
"	0.08		1.3	
"	0.44		0.36	
This study	0	14-22		
"	1.8µg/cm <sup>2</sup>			0.005-0.022

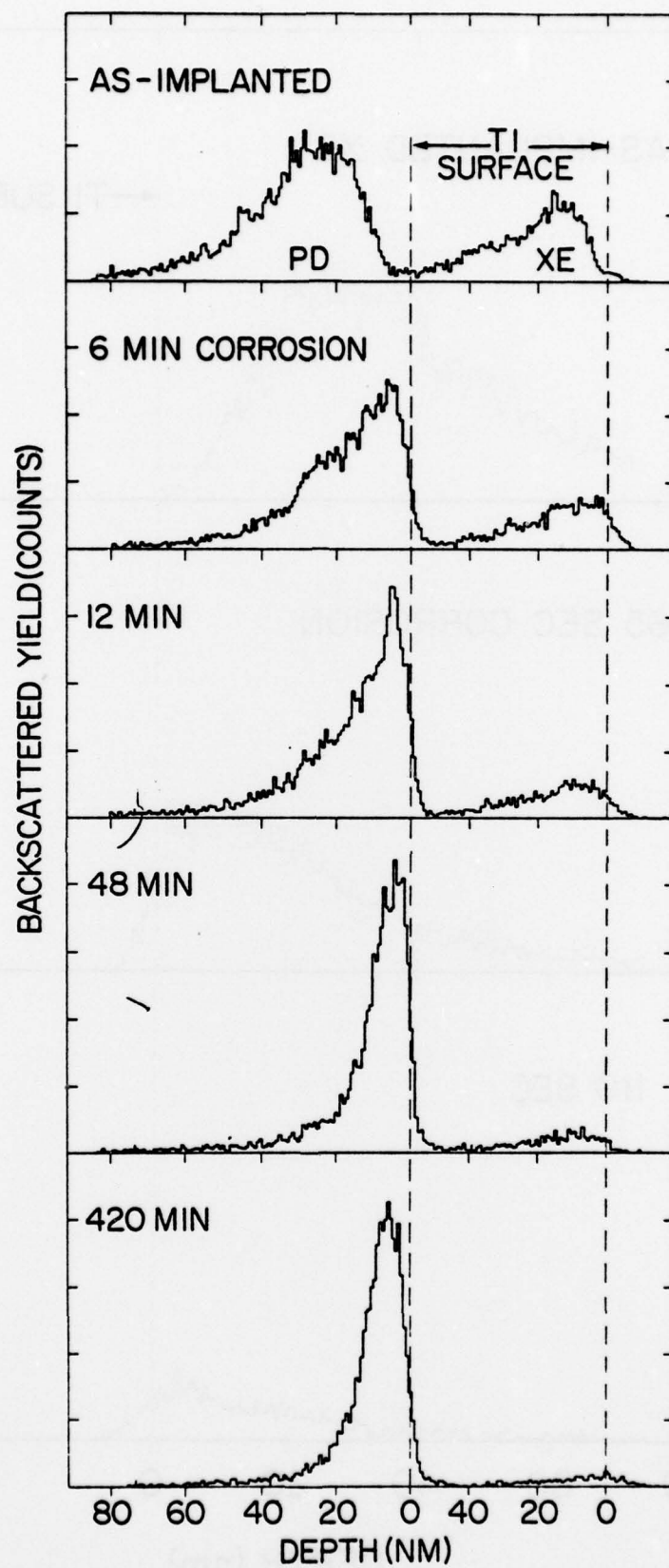


Figure 1

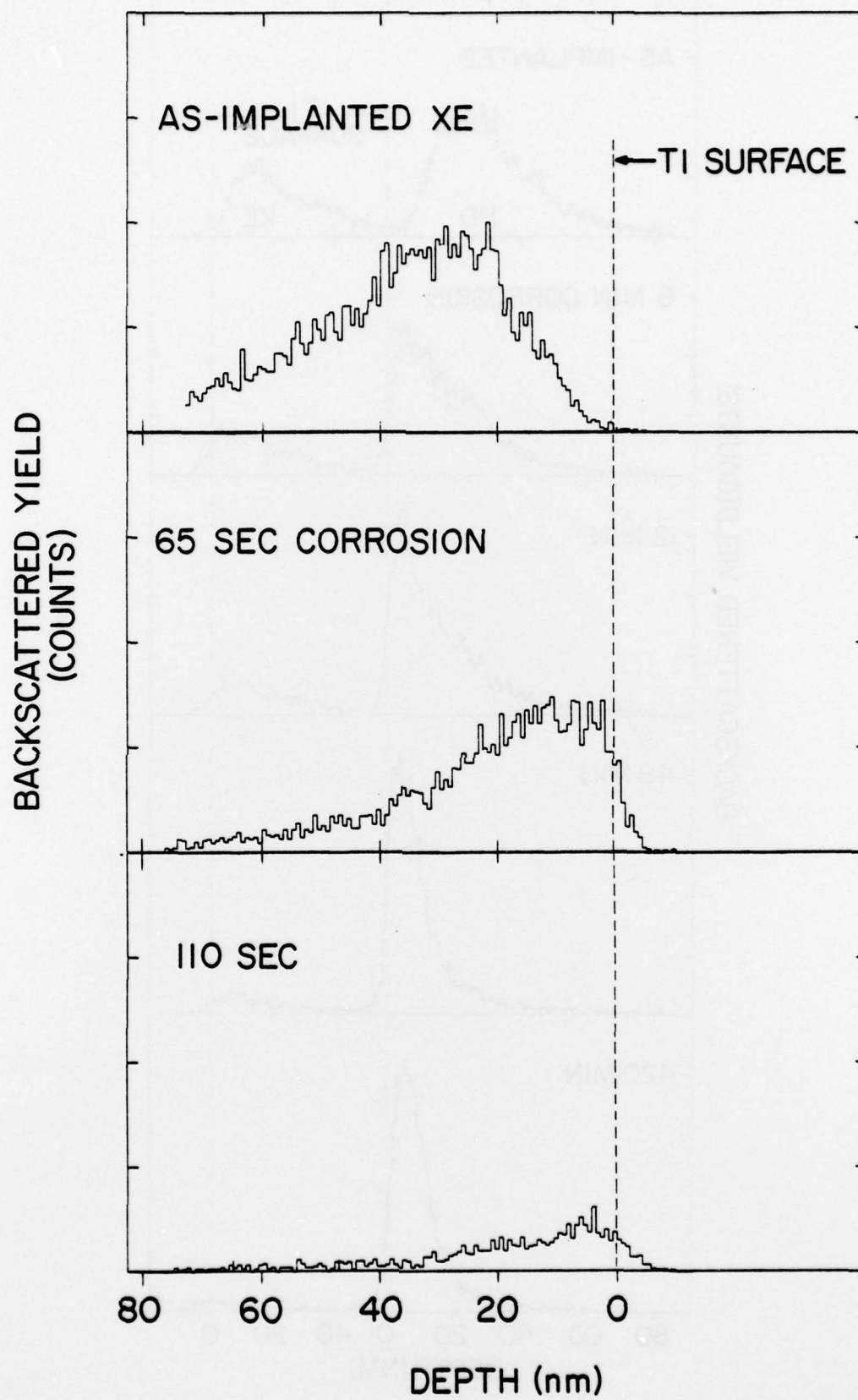


Figure 2



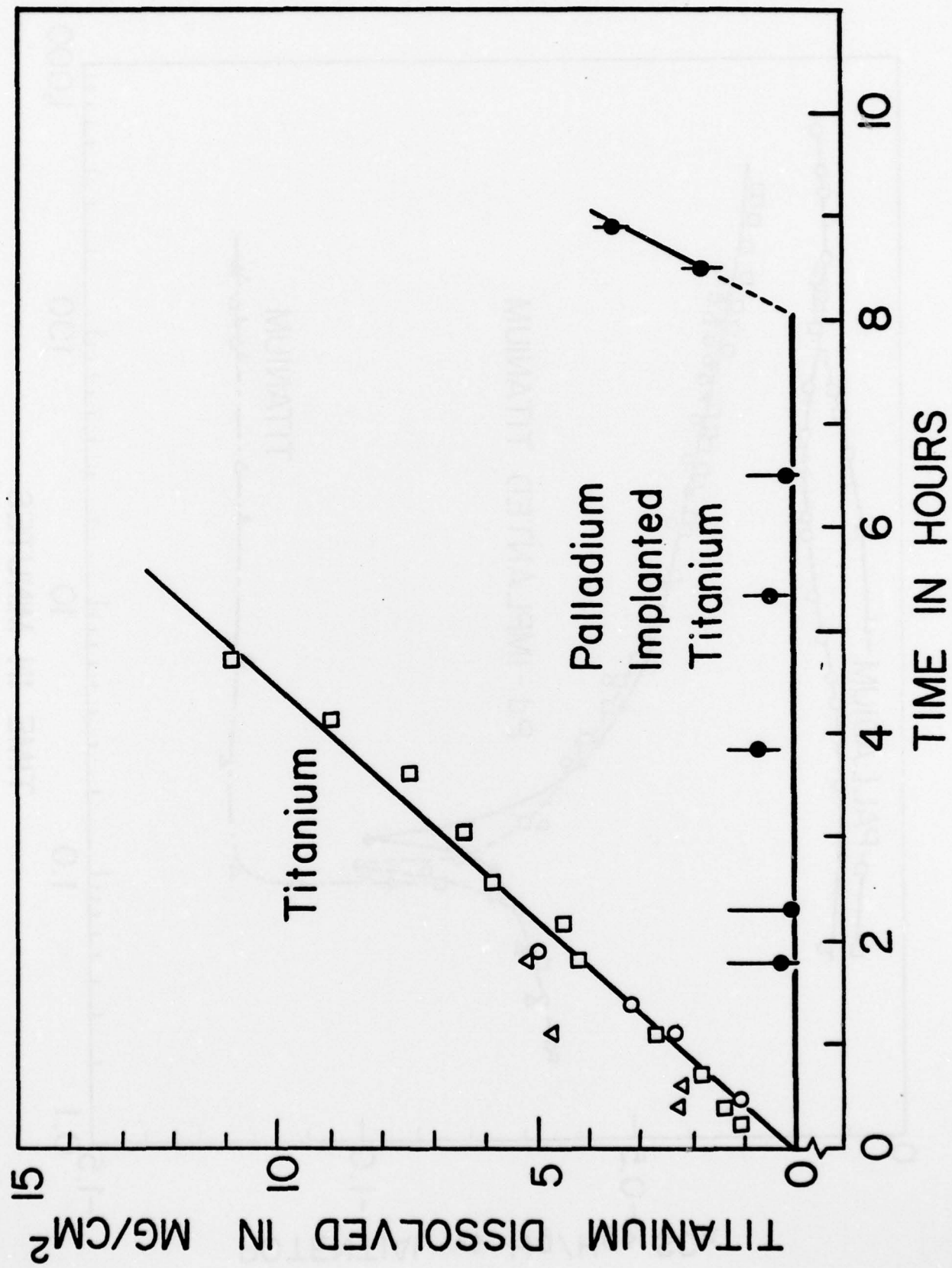


Figure 3

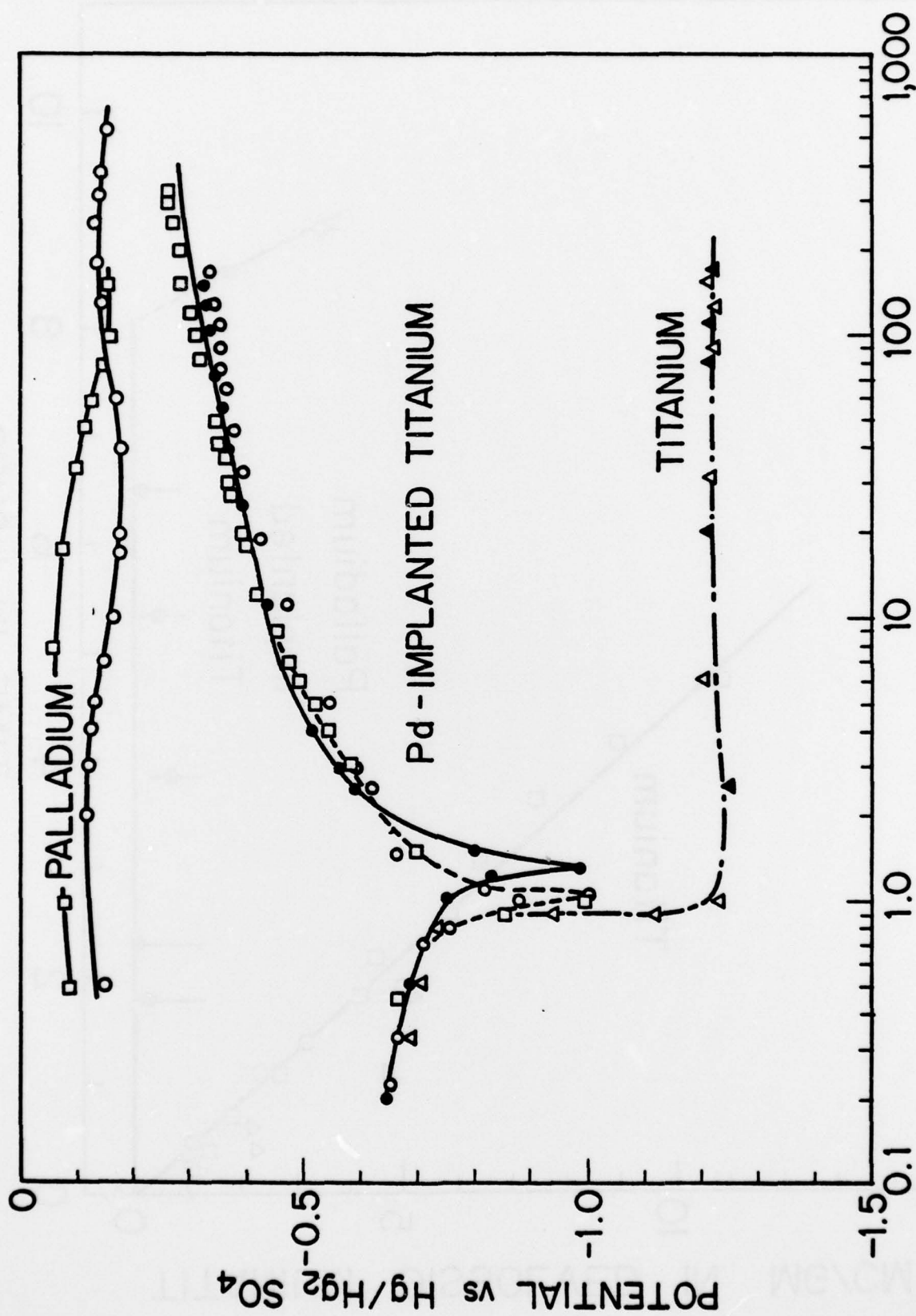


Figure 4

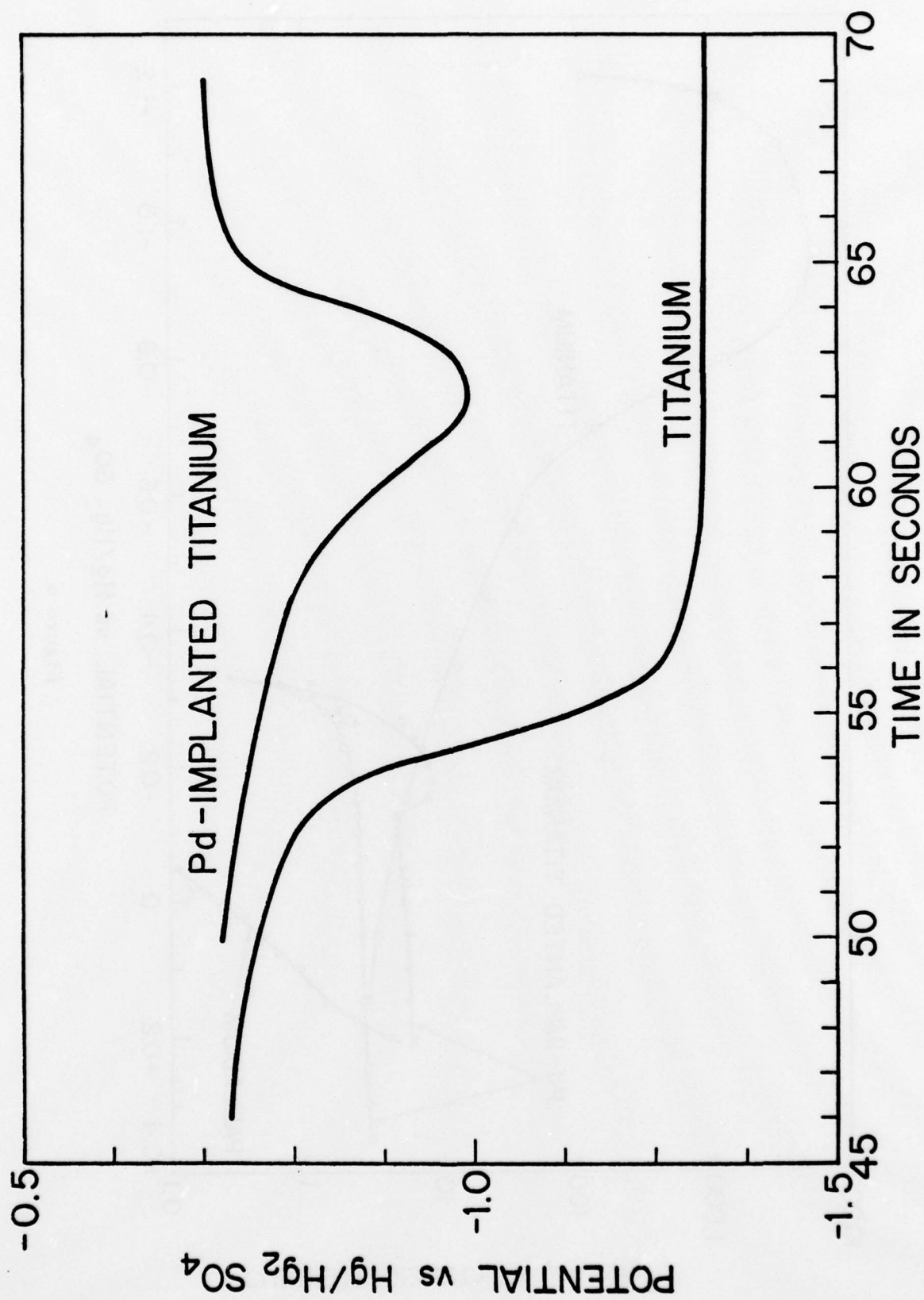


Figure 5

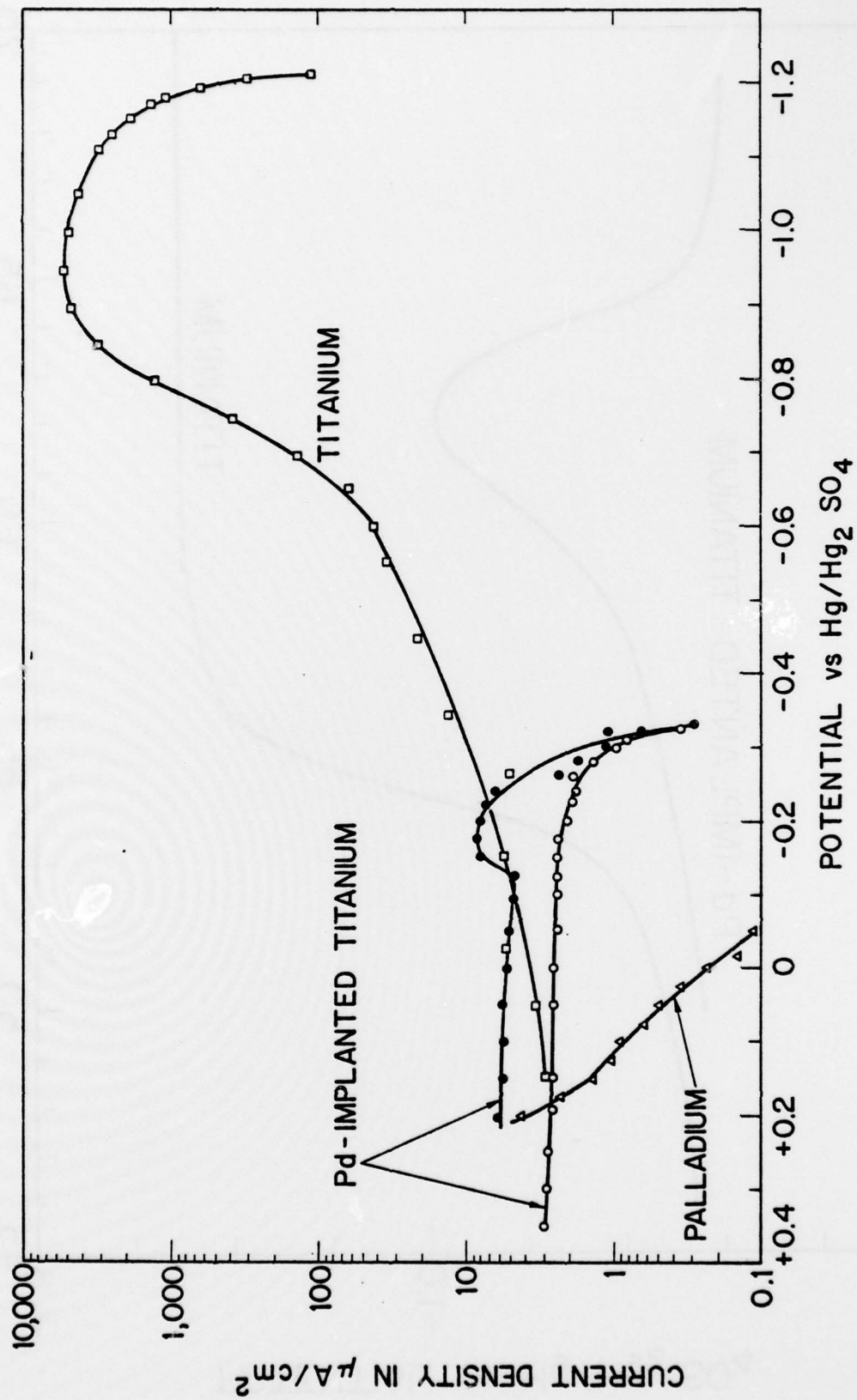


Figure 6



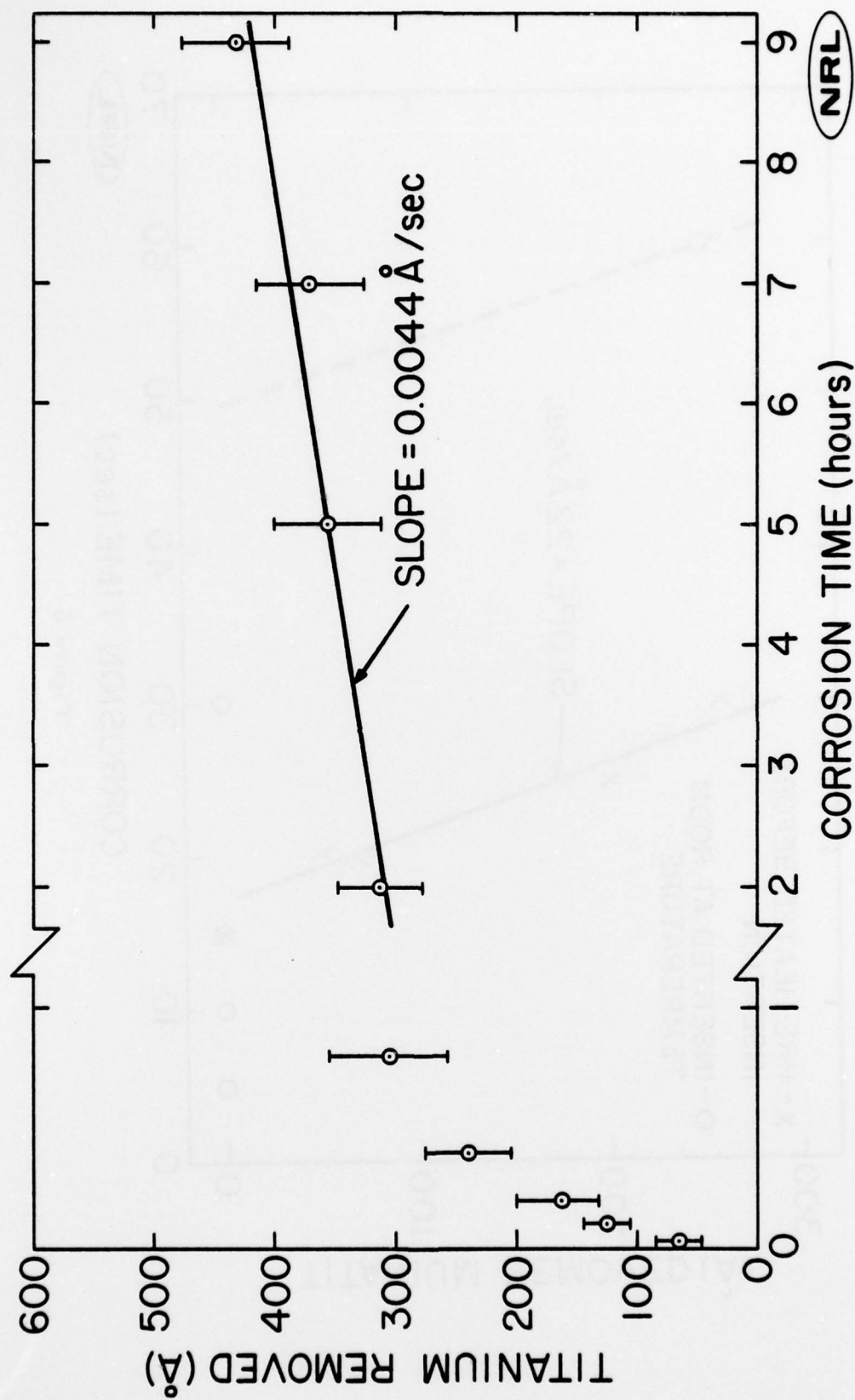


Figure 7

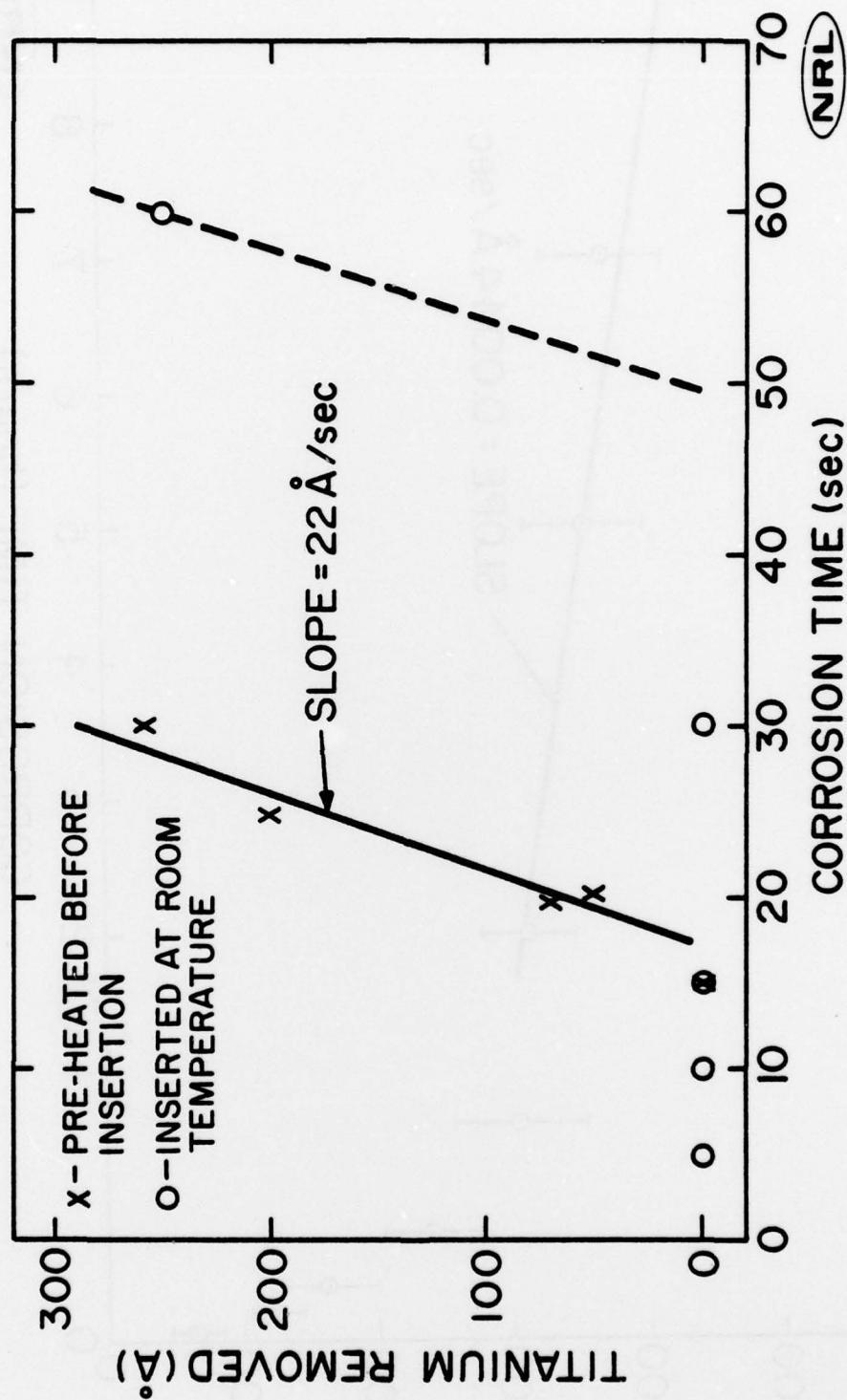
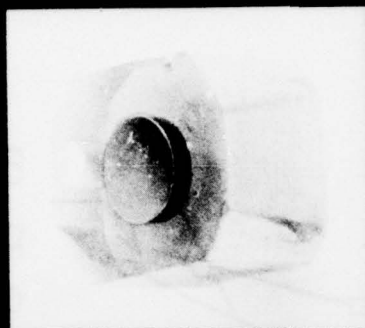


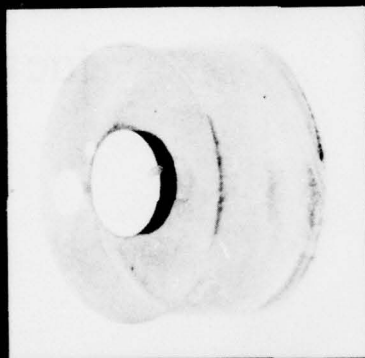
Figure 8

# CORROSION OF TITANIUM IN BOILING 1 MOLAR $H_2SO_4$

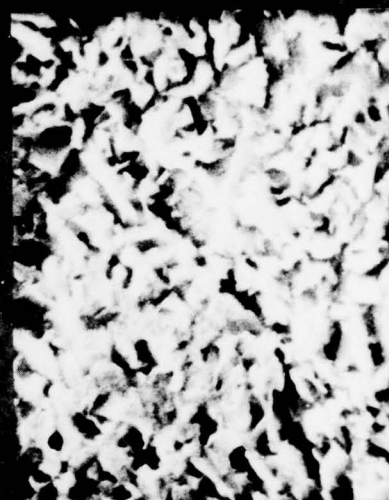
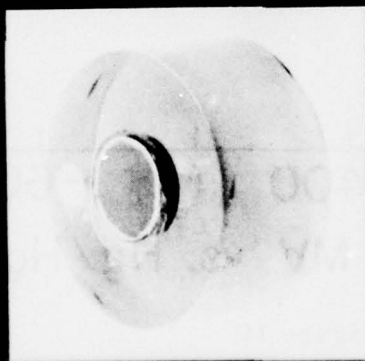
IMPLANTED ( $10^{16}$  Pd/cm<sup>2</sup>)  
48 MINUTE CORROSION



UNIMPLANTED  
8 MINUTE CORROSION



AS IMPLANTED ( $10^{16}$  Pd/cm<sup>2</sup>)



5μ



5μ

NRL

Figure 9

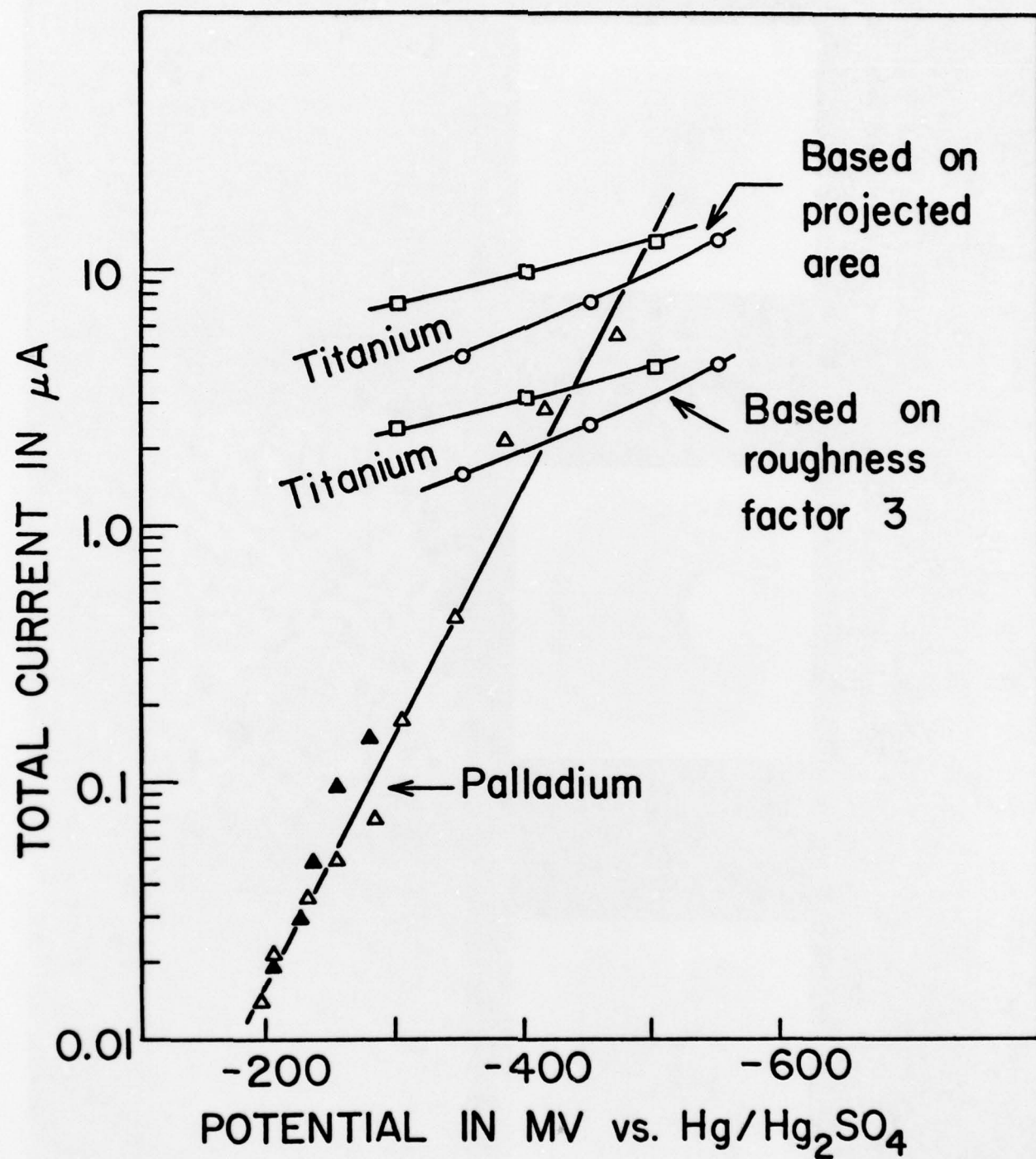


Figure 10



PUBLICATIONS AND PRESENTATIONS SPONSORED WHOLLY OR IN PART BY THIS CONTRACT

PUBLICATIONS

G.K. Hubler and E. McCafferty. "The Corrosion Behavior and Rutherford Back-scattering Analysis of Palladium Implanted Titanium," Corrosion Science, (to be published).

E. McCafferty and G.K. Hubler. "Electrochemical Behavior of Palladium-Implanted Titanium," J. Electrochem. Soc. 125 1892 (1978).

G.K. Hubler and E. McCafferty. Reports of NRL Progress, May (1978) p. 28.

E. McCafferty, G.K. Hubler, and J.K. Hirvonen. "Corrosion Control by Ion Implantation, "Proceedings of the Tri-Service Corrosion Conference, New Orleans, October (1978).

J.K. Hirvonen. "Ion Implantation in Tribology and Corrosion Science," J. Vac. Sci. & Tech. (in press).

E. A. Wolicki. "Analysis of Metal Corrosion," Proceedings of the Fifth Conference on Applications of Small Accelerators, held at North Texas State Univ., Denton, Texas, Nov. (1978) (eds. J.J. Duggan and I.L. Morgan, to be published).

#### PRESENTATIONS

- G.K. Hubler. "New Uses of Ion Implantation," Seminar, Metallurgy Dept. Pennsylvania State Univ. Dec (1976).
- G.K. Hubler. "The Corrosion Behavior and Rutherford Backscattering Analysis of Palladium-Implanted Titanium, "International Conference on Ion Implantation and Ion Beam Analysis Techniques in Corrosion, Manchester, U.K., June (1978).
- E. McCafferty. "Corrosion Control by Ion Implantation, "Tri-Service Corrosion Conference, New Orleans, October (1978).
- J.K. Hirvonen. "Ion Implantation in Tribology and Corrosion Science, "American Vacuum Society Symposium, Ion-Implantation-New Prospect for Material Modification, I.B.M. Yorktown Heights, June (1978).
- E. A. Wolicki. "Analysis of Metal Corrosion," Fifth Conference on Application of Small Accelerators, North Texas State Univ., Denton, Texas, Nov. (1978).